

(19)



Europäisches Patentamt  
European Patent Office  
Office européen des brevets



(11)

**EP 0 204 931 B2**

(12)

**NEW EUROPEAN PATENT SPECIFICATION**

(45) Date of publication and mention  
of the opposition decision:  
**14.03.2001 Bulletin 2001/11**

(51) Int Cl.7: **A61L 31/00**

(45) Mention of the grant of the patent:  
**02.08.1989 Bulletin 1989/31**

(21) Application number: **86105465.8**

(22) Date of filing: **21.04.1986**

(54) **Resorbable surgical composite material and method of producing it**

Resorbierbares chirurgisches Kompositmaterial und Verfahren zu seiner Herstellung

Matériau composite résorbable pour des implants chirurgicaux et son procédé de fabrication

(84) Designated Contracting States:  
**AT BE CH DE FR GB IT LI NL SE**

(30) Priority: **08.05.1985 FI 851828**

(43) Date of publication of application:  
**17.12.1986 Bulletin 1986/51**

(73) Proprietor: **BIOCON OY**  
**33710 Tampere (FI)**

(72) Inventors:  
• **Törmälä, Pertti**  
**SF-33730 Tampere (FI)**  
• **Rokkanen, Pentti**  
**SF-00930 Helsinki (FI)**  
• **Laiho, Juha**  
**SF-33230 Tampere (FI)**  
• **Tamminmäki, Markku**  
**SF-33400 Tampere (FI)**  
• **Vainionpää, Seppo**  
**SF-0032 Helsinki (FI)**

(74) Representative: **KEIL & SCHAAFHAUSEN**  
**Patentanwälte,**  
**Cronstettenstrasse 66**  
**60322 Frankfurt am Main (DE)**

(56) References cited:

<b>EP-B- 0 011 528</b>	<b>GB-A- 1 034 123</b>
<b>US-A- 2 703 316</b>	<b>US-A- 3 297 003</b>
<b>US-A- 3 739 773</b>	<b>US-A- 4 263 185</b>
<b>US-A- 4 279 249</b>	<b>US-A- 4 343 931</b>

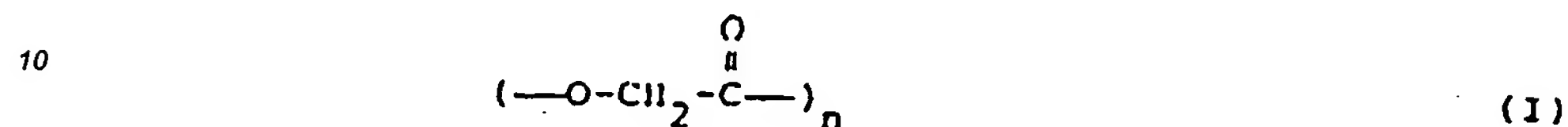
- "Biodegenerable implantate am Knochen - Idee, Realität und Zukunft" by Ian van Randenborgh, University of Würzburg, Germany, November 1983
- Römpp Chemie Lexikon, 8th Ed., Franck'sche Verlagshandlung, Stuttgart, Germany, p. 4484
- Affidavit by Prof. Pertti Törmälä with Appendix 1-8
- "Surgical applications of biodegradable polymers in human tissues" by S. Vainionpää et al, Prog. Polym. Sci. GB, vol. 14, p. 679-716, 1989
- "A new absorbable suture" by E.J. Frazza and E.E. Schmitt, J. Biomed. Mater. REs. Symposium, vol. 1, p. 53-58, 1971
- Römpp's Chemie Lexikon, 7th ed. Frank'sche Verlagshandlung, Stuttgart, Germany, p. 3297
- J. Appl. Chem. USSR, vol. 42, 1969, p. 1788-1791
- "Biocompatibility of clinical implant materials", vol. II, 1981, CRC Series in biocompatibility, p. 209-232
- Ullmann's Enzyklopädie der technischen Chemie, Verlag Chemie, vol. 19, 4th ed., 1980, p. 374-378

**EP 0 204 931 B2**

## Description

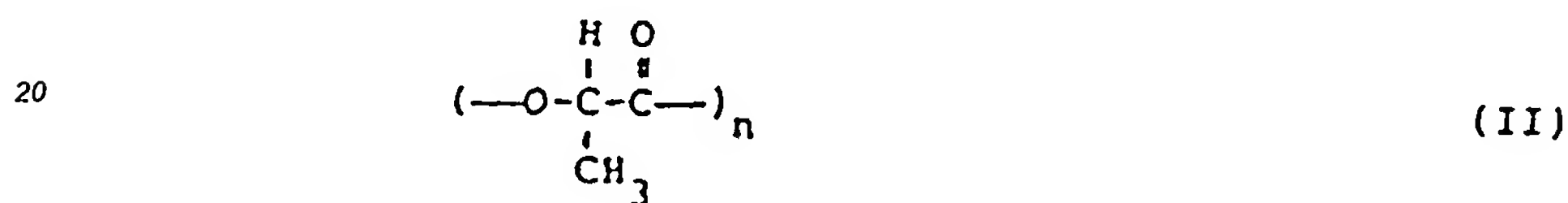
[0001] This invention relates to a synthetic, polymeric surgical osteosynthesis composite material, which is absorbable (resorbable) in tissue without causing harmful tissue reactions.

5 [0002] The manufacturing of osteosynthesis materials from absorbable polymers is known from several patents. The manufacturing of absorbable sutures and surgical elements of polyglycolide (PGA)



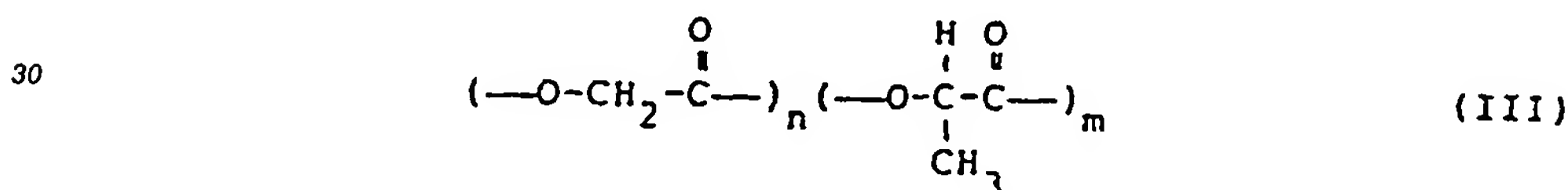
has been described in US-A-3 297 033 and US-A-3 739 773.

15 [0003] Sutures manufactured of polylactide (PLA)



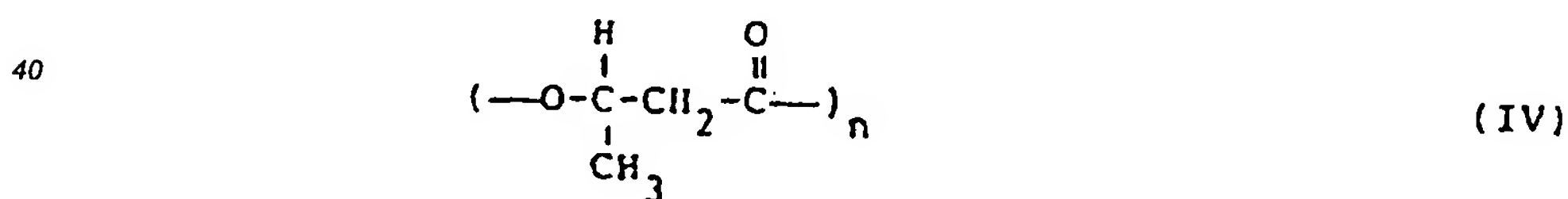
25 are described in US-A-2 703 316.

[0004] Sutures manufactured of glycolide/lactide copolymers (PGA/PLA)



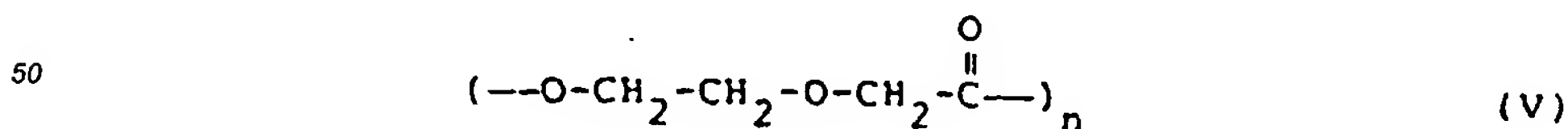
35 (where n and m are integers > 1) are described in US-A-3 839 297.

[0005] Sutures and osteosynthesis devices which are manufactured of poly-β-hydroxybutyric acid (PHB)



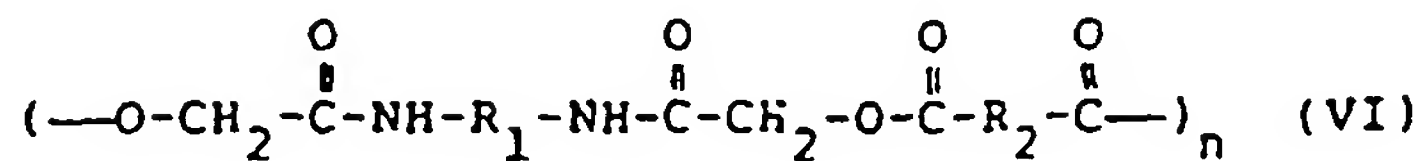
45 are described in GB-A-1 034 123.

[0006] Sutures and osteosynthesis devices which are manufactured of polydioxanone (POS)



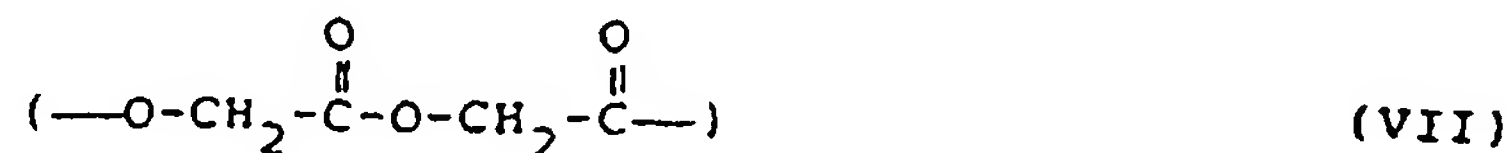
are described in US-A-4 052 988.

55 [0007] Absorbable surgical devices which are manufactured from polyesteramides (PEA)

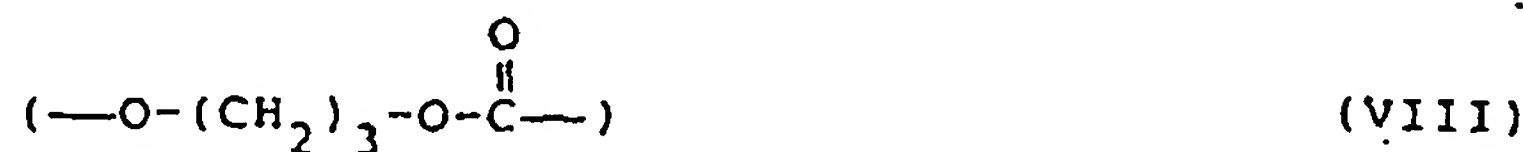


are described in US-A-4 343 931.

**[0008]** Absorbable surgical sutures and surgical devices, which are constructed of copolymer which contains units with the structural formula (VII)



as end sequences and the units with the formula (VII) combined randomly with the units (VIII)



as middle sequence, are described in FI-C-73 447.

**[0009]** Absorbable surgical devices of the above inventions are typically plates which are fixed to bone by screws, cylindrical medullary nails or corresponding structures which are manufactured by melting absorbable polymer and by moulding or pressing the melt into the suitable form. The mechanical strengths of such samples, which are manufactured by melt processing techniques, have typically the same order of magnitude as those of other similar synthetic polymers. Accordingly the tensile strengths of dry, unhydrolyzed samples manufactured from PBA, PLA, PHB and PGA/PLA have typically the order of magnitude of 40 - 80 Mpa (see e.g. Kulkarni, R.K., Moore, E.G., Hegyeli, A.F. and Fred. L. J. *Biomed. Mater. Res.*, 1971, 5, 169, Vert, M., Chabot, F. and Leray, J., *Makromol. Chem., Suppl.*, 1981, 5, 30, Christel, P., Chabot, F., Leray, J.L. Morin, C. and Vert, M., in *Biomaterials* (Eds. C.D. Winter, D.F. Gibbons and H. Plenk, Jr.), Wiley (1980), p. 271, Tunc, D.C., *Transactions of 9th Annual Meeting of the Society for Biomaterials*, Birmingham, USA, 1983, p. 47, Howells, E.R., *Chem. Ind.*, 1982, 7, 509).

**[0010]** The tensile strengths given above are modest if compared with tensile strengths of compact bone (ca. 80 - 200 Mpa). Additionally melt processed homogeneous polymeric samples of above polymers are in several cases brittle or too flexible to be applied in bone surgical applications. Therefore the conventional applications of resorbable polymers in bone surgery have encountered severe difficulties.

**[0011]** The initial mechanical strenght of surgical absorbable osteosynthesis materials has been improved by applying in absorbable polymeric matrix as reinforcement units absorbable fibers with higher melting point than that of matrix itself (e.g. polylactide matrix reinforced with polyglycolide fibers in US-A-4 279 249). Also biostable carbon fibers have been used as reinforcement units. When the chemical structure or the element composition of reinforcement units differs from that of matrix material the materials cannot form, as a rule, strong chemical primary or secondary bonds between each other which leads to poor adhesion between material components.

**[0012]** Adhesion promoters, such as silanes or titanates etc., which are usually applied in polymeric reinforced composites, cannot be applied in surgical materials intended to be used in surgery because of their toxicity. Therefore good adhesion between matrix and reinforcement units of different chemical origin is difficult to achieve.

**[0013]** From the publication "Biodegenerable Implantate am Knochen - Idee, Realität und Zukunft?" by Ian van Randenborgh, University of Würzburg, Germany, November 1983, it is known to produce pins from a polyglycolic acid material by injection molding. It is also mentioned therein that fibers of a polyglycolic acid material were incorporated into such pins by casting. Due to poor strength characteristics these pins, however, are not suitable to manufacture biodegradable implants.

**[0014]** In EP-B1-11528 there are described compositions for use in bone surgery as composite osteosynthesis pieces. The compositions consist of a matrix of polylactic acid or of a copolymer thereof which matrix contains reinforcing elements of a homopolymer or a copolymer of polyglycolic acid. Accordingly, the matrix and the reinforcing elements have different chemical element percentages.

**[0015]** J. Appl. chem. USSR, Vol. 42, 1969, pages 1788-1791, reports on self-reinforced and self-bonding materials produced from polyacrylonitrile fibers or polyvinyl alcohol fibers. The fibers are subjected to a defined pressure in a

narrow temperature range, whereby a surface monomolecular layer on the fibers is converted into the fluid state. This leads to bonding of the fibers to each other. There is no hint in that prior art that such material might be advantageous to be used for making osteosynthesis devices.

**[0016]** It is the object of the invention to provide bioabsorbable surgical osteosynthesis devices having high strength characteristics.

**[0017]** According to the invention there is provided a material as described in claim 1. The material is formed in the shape of an osteosynthesis implant from an absorbable polymer or copolymer matrix which is reinforced with absorbable reinforcement fibers having the same chemical element percentage composition as the matrix has, wherein the fiber content is at least 30% in weight. It should be noted that the matrix and reinforcement units which have the same chemical element percentage composition can be also isomers, which means that the matrix and the reinforcement units have configurations which differ from each other.

**[0018]** Preferably, the reinforcement fibers are not made of polyvinyl alcohol.

**[0019]** The present invention relates to self-reinforced absorbable polymeric surgical osteosynthesis material, which is uniform of its chemical element structure and which therefore has good adhesion between matrix and reinforcement elements. Therefore the material has excellent initial mechanical strength properties, such as high tensile, bending or shear strength and toughness, and therefore this material can be applied favourably as surgical absorbable osteosynthesis devices or as components or parts of such devices, like as osteosynthesis plates which are fixed to bone by screws, as fixing screws, as medullary nails or as components (plates, rods or barks) of such osteosynthesis devices which are described in FI-C-61 402.

**[0020]** Self-reinforcement means that the polymeric matrix is reinforced with the reinforcement units (such as fibers) which have the same chemical element percentage composition as the matrix has. By applying self-reinforcement principle the high tensile strength (typically 500 - 900 Mpa) of fibers can be effectively utilized, when manufacturing macroscopical samples. When strong oriented fiber structures are bound together with the polymer matrix which has the same chemical element composition as the fibers, the composite structure is obtained which has excellent adhesion between matrix and reinforcement units and therefore also excellent mechanical properties.

**[0021]** The annexed drawing shows schematically the structure of the material of this invention where the absorbable polymeric matrix is reinforced with the absorbable fibers.

**[0022]** The method of manufacturing said material is mainly characterized in that the part of the material which will form the matrix is subjected to heat and/or pressure in such a way that the physical condition of the part of material which will act as matrix phase allows the development of adhesion between the nearby reinforcement units and the matrix and that the material is cooled down rapidly after the development of such adhesion.

**[0023]** There are alternative methods which can be applied in manufacturing of self-reinforced absorbable

**[0024]** osteosynthesis materials of this invention. One method is to mix finely milled polymer powder with fibers, threads or corresponding reinforcement units which are manufactured of the same material or of its isomer with the same chemical element percentage composition and to heat the mixture in such conditions and using such temperatures that the finely milled particles are softened or melted but the reinforcement unit structures are not significantly softened or melted. When such composition is pressed to the suitable form the softened or melted particles form the matrix phase which binds the reinforcement units together and when this structure is cooled a self-reinforced composite with excellent adhesion and mechanical properties is obtained.

**[0025]** Self-reinforced structure of the invention is also obtained by combining together the melt of an absorbable polymer and fibers, threads or corresponding reinforcement units of the same material, forming the mixture of the polymer melt and reinforcement units into the desired form and cooling the formed polymer composite so rapidly that the reinforcement units do not lose significantly their oriented internal structure.

**[0026]** One can manufacture also the self-reinforced absorbable material of the invention by heating absorbable fibers, threads or corresponding structures in a pressurized mould in such circumstances that at least part of these structures are partially softened or melted of their surface. Under the pressure the softened or melted surfaces of fibers, threads or corresponding structures are coalesced together and when the mould is cooled a self-reinforced composite structure is obtained. By a careful control of heating conditions it is possible to process composite samples where the softened or melted surface regions of fibers, threads or corresponding units are very thin and therefore the portion of oriented fiber structure is very high leading to materials with high tensile, shear, bending and impact strength values.

**[0027]** The above manufacturing principles can be applied when the self-reinforced absorbable materials are manufactured by batch processes (such as compression moulding and transfer moulding) or by continuous processes (such as injection moulding or extrusion or pultrusion).

**[0028]** Typical properties of the materials of this invention are the high content of oriented fibers bound together with thin matrix polymer layers between fibers, low porosity, smooth and compact surface, which all properties are obtained as a consequence of application of pressure and possibly also of heat during the manufacturing of the material. Good internal adhesion properties in combination with the above advantageous structural factors give for the material excellent mechanical strength properties such as high tensile, bending, compression or impact strength.

[0029] It is natural that the self-reinforced absorbable surgical material can include, in addition to matrix and reinforcement unit polymer, necessary additives, like colours, powder-like fillers or other additives.

[0030] The self-reinforced materials of the invention can be applied in osteosynthesis implants like in surgical devices or as their components in the form of plates, pins, nails, medullary rods, screws or in the form of other three-dimensional solids. The material can form also at least part of an osteosynthesis implant. It is natural that the at least partially absorbable matrix and/or reinforcement units can contain additives such as colours, antioxidants, plasticizers, lubricants, fillers etc. which are needed in processing of the material or to modify its properties or the properties of matrix and/or reinforcement units.

[0031] When the self-reinforced material is applied as a part of surgical plate, pin, rod etc. the self-reinforced structure may form e.g. the core of the device and the surface of the device can be prepared from other material. In this way the excellent mechanical properties of self-reinforced material can be combined with properties of other absorbable materials (such as slow absorption rate).

[0032] The self-reinforced material of the invention can be applied also in several other ways in combination with other absorbable and/or biostable materials. E.g. the mechanical properties of self-reinforced material can be modified by embedding into it absorbable reinforcing units with other hydrolytic properties than those of the self-reinforced material. Composites with excellent mechanical properties are also achieved when hybrid composites of self-reinforced materials with biostable fibers (such as carbon fibers) are manufactured.

[0033] The following non-limiting examples illustrate the present invention.

#### Example 1

[0034] The melt of glycolide/lactide (90/10) copolymer (internal viscosity  $[\eta] = 1.5$  in 0.1 % hexafluoroisopropanol solution ( $T = 25^\circ \text{C}$ )) was mixed with the continuous fibers of the same material. The melt - fiber mixture was formed rapidly to cylindrical samples (diameter 4.5 mm) which were cooled rapidly and whose fiber content was 30 % (w/w). The tensile strength of these self-reinforced absorbable composite rods was 260 Mpa. The tensile strength of corresponding non-reinforced rods manufactured from glycolide/lactide copolymer melt was 50 Mpa.

#### Example 2

[0035] Glycolide/lactide copolymer sutures (Vicryl®) (size 2 USP) were heated in vacuum at  $185^\circ \text{C}$  for 6 min which caused the partial melting of fiber units of sutures. The material was compression moulded into a cylindrical mould with a pressure of 2000 bar and it was cooled rapidly. The bending strength of these self-reinforced rods was 170 Mpa. The bending strength of corresponding non-reinforced rods manufactured from glycolide/lactide copolymer melt was 90 Mpa.

#### Example 3

[0036] Polyglycolide sutures (Dexon®) (size 2 USP) were heated in pressurized cylindrical mould (length 70 mm, diameter 4.5 mm) at  $218^\circ \text{C}$  for 5 min with a pressure of 2000 bar. The softened fiber material was fused partially together and the mould was cooled to room temperature rapidly. The tensile strength of these self-reinforced absorbable composite rods was 380 Mpa. The tensile strength of corresponding non-reinforced rods manufactured from polyglycolide melt was 60 Mpa.

#### Example 4

[0037] Polyglycolide sutures (Dexon®) (size 2 USP) were melted at  $T = 230^\circ \text{C}$ . The polymer melt and corresponding continuous sutures (Dexon®) were mixed rapidly together, formed to cylindrical rods (diameter 3.2 mm) and cooled rapidly. The fiber content of self-reinforced rods was 40 % (w/w). Their tensile strength was 290 Mpa. The tensile strength of corresponding non-reinforced rods manufactured from polyglycolide melt was 60 Mpa.

#### Example 5

[0038] Isomers which can be applied to manufacture absorbable osteosynthesis devices are e.g. isomers of polylactide like poly-L-lactide (PLLA) and the DL isomer (meso lactide). PLLA is crystalline polymer with the melting point  $180^\circ \text{C}$  and the DL isomer is amorphous polymer. The self-reinforced material can be manufactured of these materials by combining DL isomer matrix and PLLA fiber, thread or corresponding reinforcement unit structures to each other by means of heat and pressure.

[0039] Bundles of poly-L-lactide (PLLA) fibers (fiber diameter  $12 \mu\text{m}$ , amount of fibers in a slightly twisted bundle =



200 pcs, molecular weight of PLLA = 100 000) and the finely powdered DL isomer (meso lactide) (molecular weight - 100 000) were mixed mechanically together and compression moulded at 165°C and 2000 bar pressure for 6 min and cooled rapidly. The fiber content of self-reinforced rods was 50 % and their tensile strength was 300 Mpa. Tensile strengths of non-reinforced rods manufactured from polymer melts were: PLLA 60 Mpa and mesolactide 55 Mpa.

#### Example 6

[0040] Self-reinforced rods of Example 3 were coated in injection moulding mould with 0.2 mm thick layer of poly-p-dioxanone melt ( $[\eta] = 0.8$  in 0.1 % tetrachloroethane solution ( $T = 25^\circ \text{C}$ ),  $T_m = 110^\circ \text{C}$ ) giving cylindrical, coated self-reinforced rods with the diameter of 4.9 mm. The bending strength of rods was 330 Mpa. After hydrolysis of three weeks in distilled water ( $T = 37^\circ \text{C}$ ) the coated self-reinforced rods had the bending strength 160 Mpa while the bending strength of non-coated self-reinforced rods was 90 Mpa.

#### Example 7

[0041] Poly-L-lactide ( $M_w = 100\,000$ ) fibers (diameter 12  $\mu\text{m}$ ) were heated in pressurized cylindrical mould (length 70 mm, diameter 4.5 mm) at 180°C for 7 min with a pressure of 2000 bar. The softened fiber material was fused partially together and the mould was cooled to room temperature rapidly. The tensile strength of these self-reinforced absorbable composite rods was 270 Mpa. The tensile strength of corresponding non-reinforced rods manufactured from poly-L-lactide melt was 50 Mpa.

#### Example 8

[0042] Poly- $\beta$ -hydroxybutyric acid ( $M_w = 80\,000$ ) fibers (diameter 15  $\mu\text{m}$ ) were heated in pressurized cylindrical mould (length 70 mm, diameter 4.5 mm) at 175°C for 5 min with a pressure of 2000 bar. The softened fiber material was fused partially together and the mould was cooled to room temperature rapidly. The tensile strength of these self-reinforced absorbable composite rods was 200 Mpa. The tensile strength of corresponding non-reinforced rods manufactured from poly- $\beta$ -hydroxybutyric acid melt was 40 Mpa.

#### Example 9

[0043] Polydioxanone sutures (PDS of Ethicon) (Size 0) were heated in pressurized cylindrical mould (length 70 mm, diameter 4.5 mm) at 103°C for 6 min with a pressure of 2000 bar. The softened fiber material was fused partially together and the mould was cooled to room temperature rapidly. The shear strength of these self-reinforced absorbable composite rods was 140 Mpa. The shear strength of corresponding non-reinforced rods manufactured from polydioxanone melt was 50 Mpa.

#### Example 10

[0044] Polyesteramide (with the chemical formula VI, where  $R_1 = R_2 = -(\text{CH}_2)_{12}-$ ;  $M_w = 60\,000$ ) fibers (diameter 12  $\mu\text{m}$ ) were heated in pressurized cylindrical mould (length 70 mm, diameter 4.5 mm) at 105°C for 4 min with a pressure of 2000 bar. The softened fiber material was fused partially together and the mould was cooled to room temperature rapidly. The shear strength of these self-reinforced absorbable composite rods was 140 Mpa. The shear strength of corresponding non-reinforced rods manufactured from polyesteramide melt was 50 Mpa.

#### Example 11

[0045] Polyglycolide sutures (Dexon®) (Size 2) mixed with 10 wt-% of carbon fibers (with diameter 6  $\mu\text{m}$ ) were heated in pressurized cylindrical mould (length 70 mm, diameter 4.5 mm) at 218°C for 5 min with a pressure of 2000 bar. The softened polyglycolide fiber material was fused partially together and the mould was cooled to room temperature rapidly. The tensile strength of this self-reinforced absorbable hybride composite material containing carbon fibers was 450 Mpa. The tensile strength of the corresponding carbon fiber reinforced material manufactured from polyglycolide melt - carbon fiber mixture was 160 Mpa.

#### Example 12

[0046] Glycolide/lactide copolymer sutures (Vicryl®) containing 10 wt-% of polyglycolide sutures (Dexon®) (Size 2) were heated in vacuum at 185°C for 6 min which caused the partial melting of glycolide/lactide fiber units of Vicryl®

sutures. The material was compression moulded in a cylindrical mould (length 70 mm, diameter 4.5 mm) with a pressure of 2000 bar and it was cooled rapidly. A hybride composite rod which was composed of self-reinforced glycolide/lactide material into which were embedded polyglycolide sutures was obtained. The bending strength of hybride composite material was 240 Mpa. The bending strength of corresponding composite manufactured from glycolide/lactide copolymer melt reinforced with 10 wt-% of polyglycolide sutures was 150 Mpa.

### Example 13

[0047] Monofilament sutures (size 0) manufactured from polyglycolide/trimethylenecarbonate copolymer (Maxon of Davis + Geck) were heated in a pressurized cylindrical mould (length 50 mm, diameter 3.2 mm) at 180°C for 8 min with a pressure of 2000 bar. The sutures were partially fused together and the mould was cooled to room temperature rapidly. Self-reinforced absorbable rods with the shear strength of 110 Mpa were obtained. The shear strength of corresponding non-reinforced rods manufactured from totally melted Maxon sutures was 60 Mpa.

### Claims

1. Surgical osteosynthesis composite material formed in the shape of an osteosynthesis implant or part thereof, wherein the composite material is at least partially absorbable in tissue conditions,

wherein the composite material is self-reinforced, i.e. is formed from an absorbable polymer and copolymer matrix which is reinforced with absorbable polymeric reinforcement fibers having essentially the same chemical element percentage composition as the matrix has, and

wherein the fiber content in the self-reinforced material is at least 30% in weight.

2. Material according to claim 1, wherein the polymer or copolymer from which the reinforcement fibers are manufactured is not polyvinyl alcohol (PVA).

3. Material according to claim 1, wherein the polymer or copolymer from which the reinforcement fibers are manufactured is selected from the group consisting of

- polyglycolide (PGA) or its copolymer
- polylactide (PLA) or its copolymer
- glycolide / lactide copolymer
- poly- $\beta$ -hydroxybutyric acid (PHB)
- polydioxanone (PDS)
- polyesteramide (PEA).

4. Material according to any of claims 1 to 3, wherein the fibers are provided in the form of threads, twists, cords, ribbons, or woven fabrics.

5. Material according to any of claims 1 to 4, wherein it is formed in the shape of a plate, pin, nail, medullary rod, or screw.

6. Use of a surgical osteosynthesis composite material which is at least partially absorbable in tissue conditions and which is self-reinforced, i.e. is formed from a polymer or copolymer matrix reinforced with absorbable polymeric reinforcement fibers having essentially the same chemical element percentage composition as the matrix has, to manufacture a surgical osteosynthesis implant or part thereof having a fiber content of at least 30% in weight.

7. Method for manufacturing material for osteosynthesis implants or parts thereof in accordance with any of claims 1 to 5, characterized in that the part of the material which will form the matrix is subjected to heat and/or pressure in such a way that the physical condition of the part of material which will act as matrix phase allows the development of adhesion between the nearby reinforcement fibers and the matrix and that the material is cooled rapidly after the development of such adhesion.

8. Method for manufacturing material as claimed in claim 7, characterized in that the melt of absorbable polymer or copolymer and the absorbable reinforcement fibers are mixed together, the mixture is formed into the desired

shape and cooled down rapidly.

9. Method for manufacturing material as claimed in claim 8, characterized in that the absorbable fiber, thread, twist, cord, ribbon, or woven fabric is heated in such a way that the material is softened or melted and coalesced at least partially and the material is formed into the desired shape by means of pressure and cooled down rapidly.

#### Patentansprüche

1. Chirurgisches Kompositmaterial zur Osteosynthese, das in Gestalt eines Osteosyntheseimplantates oder eines Teiles desselben geformt ist, wobei das Kompositmaterial unter Gewebebedingungen mindestens teilweise resorbierbar ist,
 

wobei das Kompositmaterial eigenverstärkt ist, d.h. aus einer resorbierbaren Polymer- und Copolymermatrix geformt ist, die mit resorbierbaren polymeren Verstärkungsfasern mit im Wesentlichen der gleichen prozentualen atomaren Zusammensetzung wie die Matrix eigenverstärkt ist, und

wobei der Fasergehalt in dem eigenverstärkten Material wenigstens 30 Gewichtsprozent beträgt.
2. Material nach Anspruch 1, wobei das Polymer oder Copolymer, aus dem die Verstärkungsfasern hergestellt sind, nicht Polyvinylalkohol (PVA) ist.
3. Material nach Anspruch 1, wobei das Polymer oder Copolymer, aus dem die Verstärkungsfasern hergestellt sind, aus der Gruppe ausgewählt wird, die aus
  - Polyglycolid (PGA) oder seinen Copolymeren
  - Polylactid (PLA) oder seinen Copolymeren
  - Glycolid/Lactid-Copolymer
  - Poly- $\beta$ -Hydroxybuttersäure (PHB)
  - Polydioxanon (PDS)
  - Polyesteramid (PEA)
 besteht.
4. Material nach einem der Ansprüche 1 bis 3, wobei die Fasern in Form von Fäden, Garnen, Schnüren, Bändern oder gewebten Strukturen vorgesehen sind.
5. Material nach einem der Ansprüche 1 bis 4, wobei es in Gestalt einer Platte, eines Stiffes, eines Nagels, eines Knochenmarkstabes oder einer Schraube geformt ist.
6. Verwendung eines chirurgischen Kompositmaterials zur Osteosynthese, das unter Gewebebedingungen wenigstens teilweise resorbierbar und das eigenverstärkt ist, d.h. aus einer Polymer- oder Copolymermatrix geformt ist, die durch resorbierbare polymere Verstärkungsfasern mit im Wesentlichen der gleichen chemischen prozentualen Zusammensetzung wie die Matrix verstärkt ist, zur Herstellung eines chirurgischen Osteosyntheseimplantates oder eines Teiles desselben mit einem Fasergehalt von wenigstens 30 Gewichtsprozent.
7. Verfahren zur Herstellung eines Materials für Osteosyntheseimplantate oder Teile derselben gemäß einem der Ansprüche 1 bis 5, **dadurch gekennzeichnet**, dass der Teil des Materials, welcher zur Matrix wird, Wärme und/oder Druck derart ausgesetzt wird, dass die physikalischen Eigenschaften des Teiles des Materials, der als Matrixphase dient, eine Haftung zwischen benachbarten Verstärkungsfasern und der Matrix erlauben, und dass das Material nach der Entwicklung dieser Haftung schnell abgekühlt wird.
8. Verfahren zur Herstellung von Material nach Anspruch 7, **dadurch gekennzeichnet**, dass die Schmelze des resorbierbaren Polymers oder Copolymers und die resorbierbaren Verstärkungsfasern zusammengemischt werden, dass die Mischung zu der gewünschten Gestalt geformt wird und schnell abgekühlt wird.
9. Verfahren zur Herstellung von Material nach Anspruch 8, **dadurch gekennzeichnet**, dass die resorbierbare Faser, Faden, Garn, Schnur, Band oder gewebte Struktur derart erwärmt wird, dass das Material erweicht oder geschmol-



zen wird und wenigstens teilweise zusammenwächst, und dass das Material durch Druck in die gewünschte Gestalt geformt und schnell abgekühlt wird.

## 5 Revendications

1. Matériau composite chirurgical d'ostéosynthèse formé en configuration d'un implant ostéosynthèse ou d'une partie de celui-ci, dans lequel le matériau composite est absorbable, au moins partiellement, dans les conditions tissulaires,

dans lequel le matériau composite est auto-renforcé, c'est-à-dire qu'il est constitué par une matrice de polymère ou de copolymère absorbable qui est renforcée par des fibres de renfort en polymère absorbable qui ont essentiellement la même composition en pourcentage d'éléments chimiques que la matrice, et

dans lequel le teneur en fibre dans le matériau auto-renforcé est au moins 30% en poids.

2. Matériau selon la revendication 1, dans lequel le polymère ou copolymère duquel les fibres de renfort sont faites n'est pas l'alcool polyvinylique (PVA).

3. Matériau selon la revendication 1, dans lequel le polymère ou copolymère duquel les fibres de renfort sont faites et choisi de la groupe consistante de

- polyglycolide (PGA) ou d'un copolymère de celui-ci
- polylactide (PLA) ou d'un copolymère de celui-ci
- copolymère glycolide/lactide
- poly- $\beta$ -hydroxybutyrique (PHB)
- polydioxanone (PDS)
- polyesteramide (PEA).

4. Matériau selon l'une quelconque des revendications 1 à 3, dans lequel les fibres se présentent sous la forme de fils, de fils retordus, de cordons, de rubans ou de tissus.

5. Matériau selon l'une quelconque des revendications 1 à 4, dans lequel il est formé en configuration d'une plaque, une cheville, un clou, une broche médullaire ou une vis.

6. Usage d'un matériau composite chirurgical d'ostéosynthèse qui est absorbable, au moins partiellement, dans les conditions tissulaires, et qui est auto-renforcé, c'est-à-dire qu'il est constitué par une matrice de polymère ou de copolymère absorbable qui est renforcée par des fibres de renfort en polymère absorbable qui ont essentiellement la même composition en pourcentage d'éléments chimiques que la matrice, pour faire un implant d'ostéosynthèse ou une partie de celui-ci qui a un teneur de fibres de au moins 30% en poids.

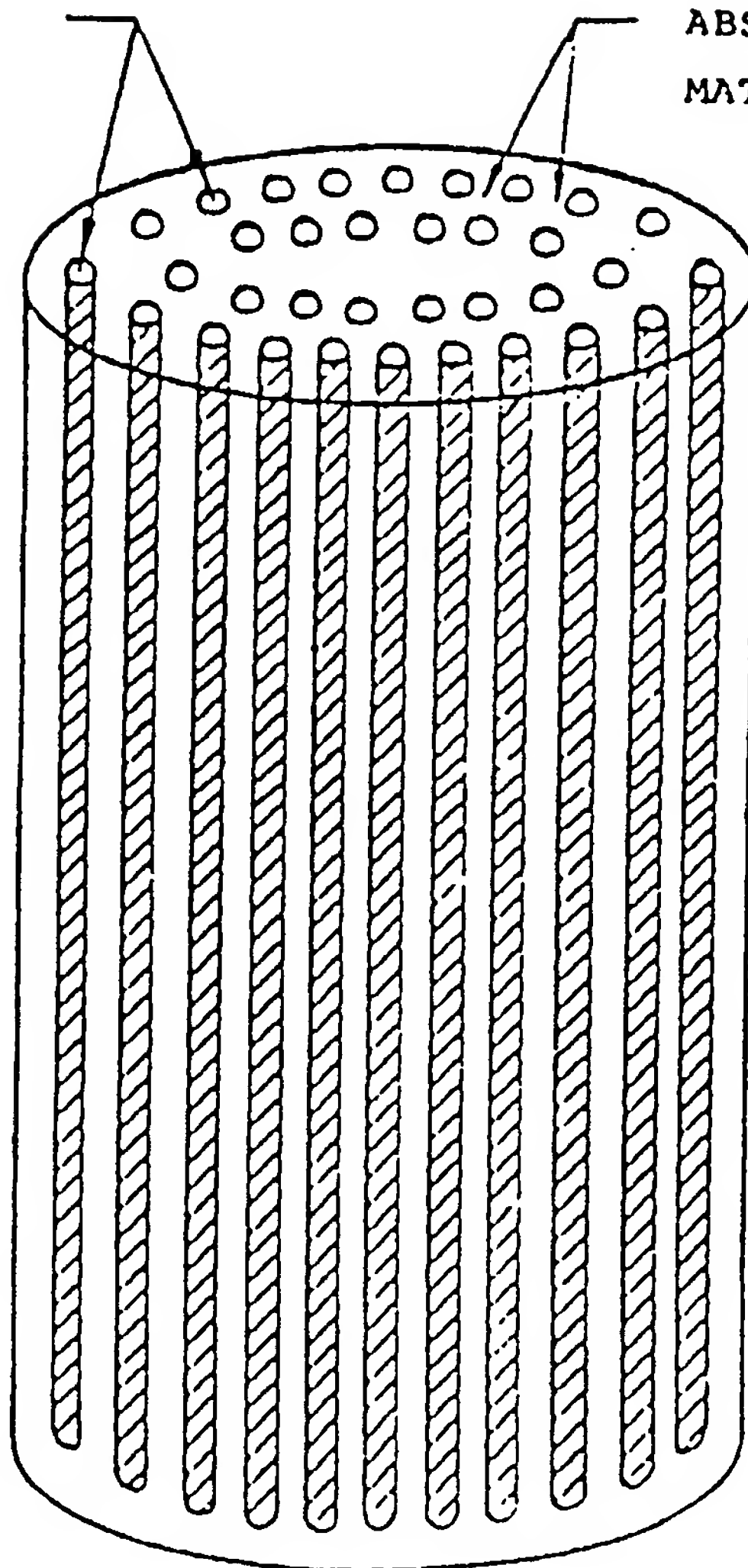
7. Procédé de fabrication d'un matériau pour des implants d'ostéosynthèse ou pour des parties de celui-ci selon l'une quelconque des revendications 1 à 5, caractérisé en ce que la partie du matériau qui formera la matrice est soumise à la chaleur et/ou à la pression, de telle façon que l'état physique de la partie du matériau qui servira de phase de matrice permette le développement d'adhérence entre les fibres de renfort contigues et la matrice, et en ce que le matériau est refroidi rapidement après la développement d'adhérence.

8. Procédé de fabrication de matériau selon la revendication 7, caractérisé en ce que la masse fondue de polymère ou de copolymère absorbable et les fibres de renfort absorbables sont mélangées ensemble, puis le mélange est mis sous la forme voulue et refroidi rapidement.

9. Procédé de fabrication de matériau selon la revendication 8, caractérisé en ce que le fibre, le fil, le fil retordu, le cordon, le ruban et le tissus absorbable est chauffé de telle manière qu'il soit ramolli ou fondu et aggloméré au moins partiellement, puis le matériau est mis sous la forme voulue par application de pression et refroidi rapidement.

ABSORBABLE  
FIBERS

ABSORBABLE  
MATRIX





Europäisches Patentamt  
European Patent Office  
Office européen des brevets

Publication number:

**0 204 931  
B1**

(12)

## EUROPEAN PATENT SPECIFICATION

(45) Date of publication of the patent specification:  
**02.08.89**

(51) Int. Cl.: **A 61 L 31/00**

(21) Application number: **86105465.8**

(22) Date of filing: **21.04.86**

(54) **Resorbable surgical composite material and method of producing it.**

(30) Priority: **08.05.85 FI 851828**

(43) Date of publication of application:  
**17.12.86 Bulletin 86/51**

(45) Publication of the grant of the patent:  
**02.08.89 Bulletin 89/31**

(84) Designated Contracting States:  
**AT BE CH DE FR GB IT LI NL SE**

(56) References cited:  
**EP-A-0 146 398  
WO-A-84/03035  
DE-A-2 917 446  
DE-A-2 947 985  
DE-A-3 245 633**

(73) Proprietor: **BIOCON OY, Runeberginkatu 3 A 1, SF-33710 Tampere (FI)**

(72) Inventor: **Törmälä, Pertti, Reikonkatu 7 C 7, SF-33730 Tampere (FI)**  
Inventor: **Rokkanen, Pentti, Marjaniemenranta 29, SF-00930 Helsinki (FI)**  
Inventor: **Laiho, Juha, Pirkankatu 20 B 1, SF-33230 Tampere (FI)**  
Inventor: **Tamminmäki, Markku, Kukkolankatu 23, SF-33400 Tampere (FI)**  
Inventor: **Vainionpää, Seppo, Orapihlajatie 21-27 B 12, SF-0032 Helsinki (FI)**

(74) Representative: **Siebmans, Hubertus, Götalands Patentbyrå AB Box 154, S-561 22 Huskvarna (SE)**

**EP 0 204 931 B1**

Note: Within nine months from the publication of the mention of the grant of the European patent, any person may give notice to the European Patent Office of opposition to the European patent granted. Notice of opposition shall be filed in a written reasoned statement. It shall not be deemed to have been filed until the opposition fee has been paid (Art. 99(1) European patent convention).

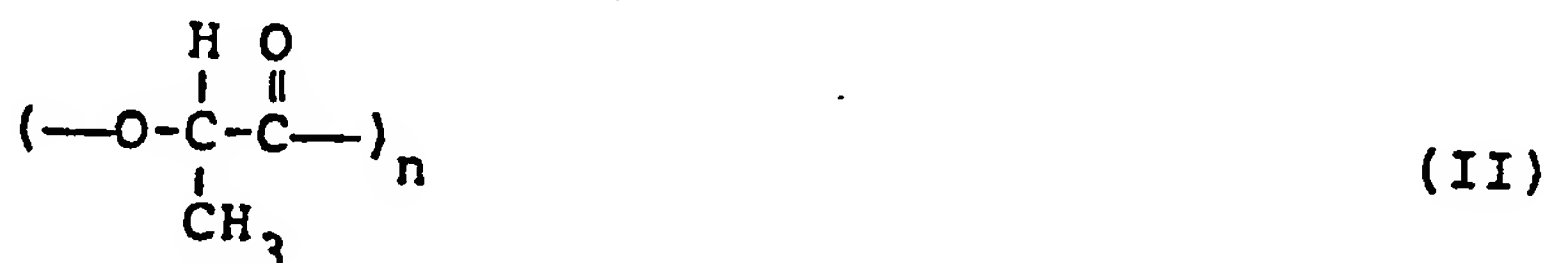
## Description

This invention relates to synthetic, polymeric surgical osteosynthesis composite material, which is absorbable (resorbable) in tissue without causing harmful tissue reactions. This material can be applied to manufacture osteosynthesis devices or their components plates, balks, rods, medillary nails, pins, screws or corresponding.

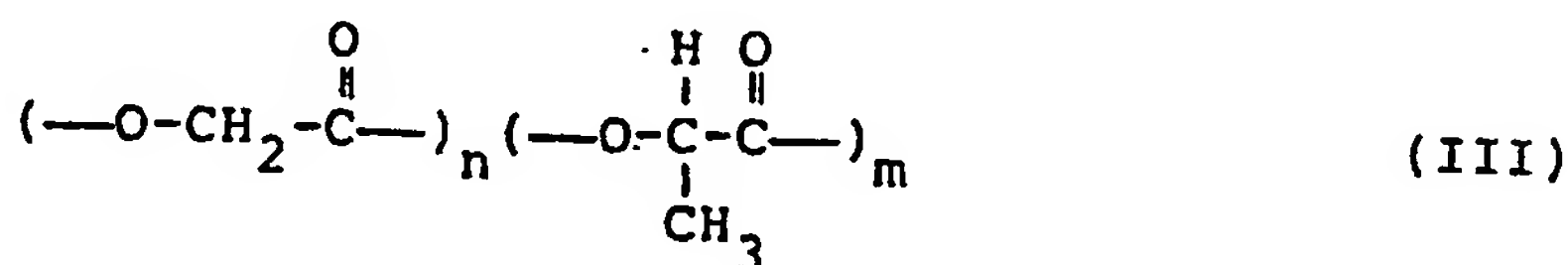
The manufacturing of osteosynthesis materials about absorbable polymers is known about several patents. The manufacturing of absorbable sutures and surgical elements of polyglycolide (PGA)



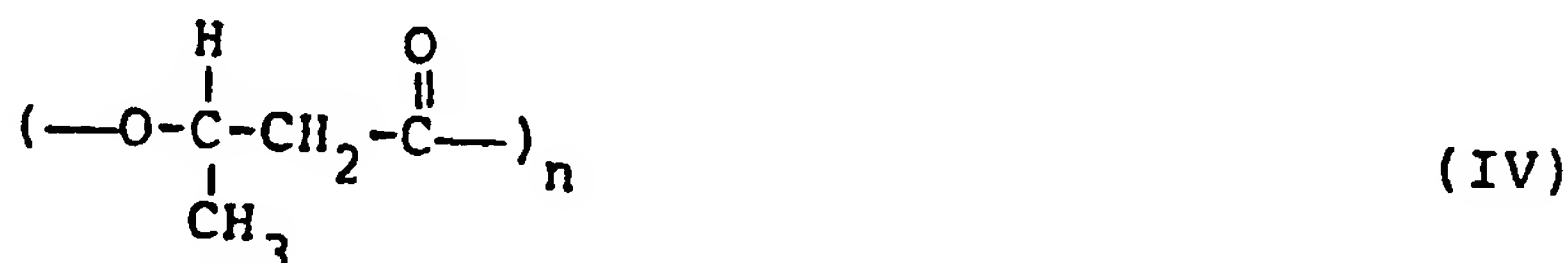
has been described in US-A-3 297 033 and US-A-3 739 773.  
Sutures manufactured of polylactide (PLA)



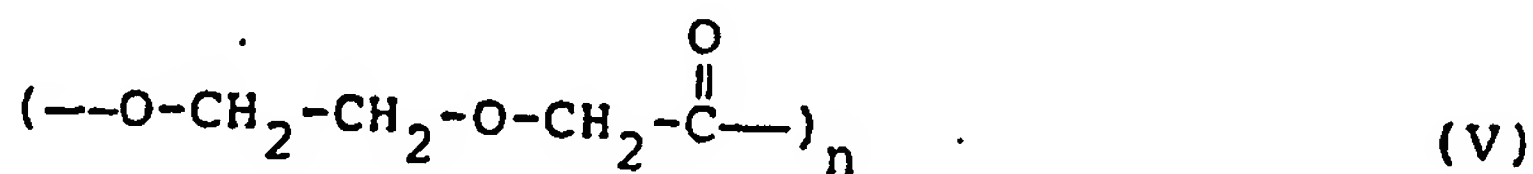
are described in US-A-2 703 316.  
Sutures manufactured of glycolide/lactide copolymers (PGA/PLA)



(where n and m are integers > 1) are described in US-A-3 839 297.  
Sutures and osteosynthesis devices which are manufactured of poly-β-hydroxybutyric acid (PHB)

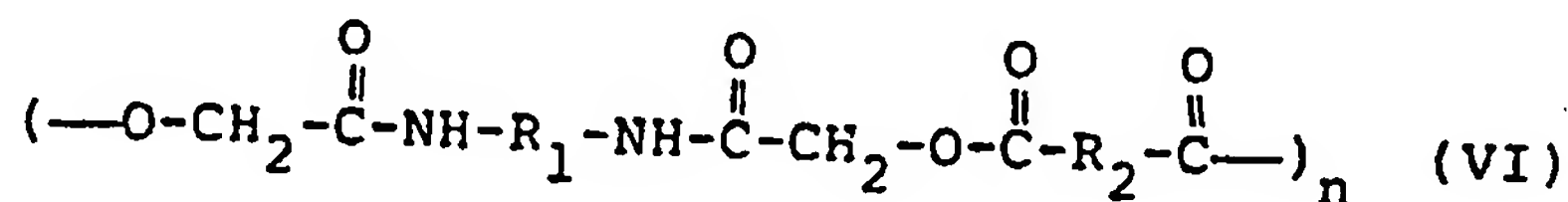


are described in GB-A-1 034 123.  
Sutures and osteosynthesis devices which are manufactured of polydioxanone (PDS)



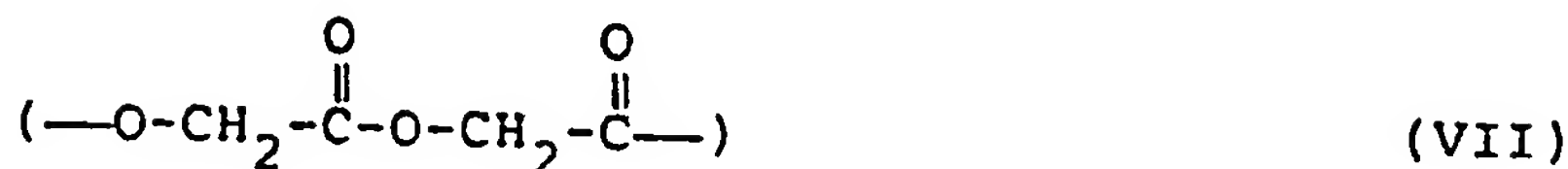
are described in US-A-4 052 988.

Absorbable surgical devices which are manufactured about polyesteramides (PEA)



are described in US-A-4 343 931.

Absorbable surgical sutures and surgical devices, which are constructed of copolymer which contains units with the structural formula (VII)



as end sequences and the units with the formula (VII) combined randomly with the units (VIII)



as middle sequence, are described in FI-C-73 447.

Absorbable surgical devices of the above inventions are typically plates which are fixed to bone by screws, cylindrical medullary nails or corresponding structures which are manufactured by melting absorbable polymer and by moulding or pressing the melt into the suitable form. The mechanical strengths of such samples, which are manufactured by melt processing techniques, have typically the same order of magnitude as those of other similar synthetic polymers. Accordingly the tensile strengths of dry, unhydrolyzed samples manufactured about PBA, PLA, PHB and PGA/PLA have typically the order of magnitude of 40 - 80 Mpa (see e.g. Kulkarni, R.K., Moore, E.G., Hegyeli, A.F. and Fred, L., *J. Biomed. Mater. Res.*, 1971, 5, 169, Vert, M., Chabot, F. and Leray, J., *Makromol. Chem., Suppl.*, 1981, 5, 30, Christel, P., Chabot, F., Leray, J.L., Morin, C. and Vert, M., in *Biomaterials* (Eds. C.D. Winter, D.F. Gibbons and H. Plenk, Jr.), Wiley (1980), p. 271, Tunc, D.C., *Transactions of 9th Annual Meeting of the Society for Biomaterials*, Birmingham, USA, 1983, p. 47, Howells, E.R., *Chem. Ind.*, 1982, 7, 509).

The tensile strengths given above are modest if compared with tensile strengths of compact bone (ca. 80 - 200 Mpa). Additionally melt processed homogeneous polymeric samples of above polymers are in several cases brittle or too flexible to be applied in bone surgical applications. Therefore the conventional applications of resorbable polymers in bone surgery have encountered severe difficulties.

The initial mechanical strength of surgical absorbable osteosynthesis materials has been improved by applying in absorbable polymeric matrix as reinforcement units absorbable fibers with higher melting point than that of matrix itself (e.g. polylactide matrix reinforced with polyglycolide fibers in US-A-4 279 249). Also biostable carbon fibers have been used as reinforcement units. When the chemical structure or the element composition of reinforcement units differs from that of matrix material the materials cannot form, as a rule, strong chemical primary or secondary bonds between each other which leads to poor adhesion between material components.

Adhesion promoters, such as silanes or titanates etc., which are usually applied in polymeric reinforced composites, cannot be applied in surgical materials intended to be used in surgery because of their toxicity. Therefore good adhesion between matrix and reinforcement units of different chemical origin is difficult to achieve.

The invention is mainly characterized in that the osteosynthesis material is self-reinforced i.e. it is formed of the absorbable polymer or copolymer matrix which is reinforced with the absorbable reinforcement units which have the same chemical element percentage composition as the matrix has. It should be also noted that the matrix and reinforcement units which have the same chemical element percentage composition can be also isomers, which means that the matrix and the reinforcement units have configurations which differ from each other.

The present invention relates to self-reinforced absorbable polymeric surgical osteosynthesis material, which is uniform of its chemical element structure and which therefore has good adhesion between matrix and reinforcement elements. Therefore the material has excellent initial mechanical strength properties, such as high tensile, bending or shear strength and toughness, and therefore this material can be applied favourably as surgical absorbable osteosynthesis devices or as components or parts of such devices, like as osteosynthesis plates which are fixed to bone by screws, as fixing screws, as medullary nails or as components (plates, rods or barks) of such osteosynthesis devices which are described in FI-C-61 402.

Self-reinforcement means that the polymeric matrix is reinforced with the reinforcement units (such as fibers) which have the same chemical element percentage composition as the matrix has. By applying self-reinforcement principle the high tensile strength (typically 500 - 900 Mpa) of fibers can be effectively utilized, when manufacturing macroscopical samples. When strong oriented fiber structures are bound together with the polymer matrix which has the same chemical element composition as the fibers, the composite structure is obtained which has excellent adhesion between matrix and reinforcement units and therefore also excellent mechanical properties.

The annexed drawing shows schematically the structure of the material of this invention where the absorbable polymeric matrix is reinforced with the absorbable fibers.

Method is mainly characterized in that the part of the material which will form the matrix is subjected to heat and/or pressure in such a way that the physical condition of the part of material which will act as matrix phase allows the development of adhesion between the nearby reinforcement units and the matrix.

There are alternative methods which can be applied in manufacturing of self-reinforced absorbable



osteosynthesis materials of this invention. One method is to mix finely milled polymer powder with fibers, threads or corresponding reinforcement units which are manufactured of the same material or of its isomer with the same chemical element percentage composition and to heat the mixture in such conditions and using such temperatures that the finely milled particles are softened or melted but the reinforcement unit structures are not significantly softened or melted. When such composition is pressed to the suitable form the softened or melted particles form the matrix phase which binds the reinforcement units together and when this structure is cooled a self-reinforced composite with excellent adhesion and mechanical properties is obtained.

Self-reinforced structure of the invention is also obtained by combining together the melt of an absorbable polymer and fibers, threads or corresponding reinforcement units of the same material, forming the mixture of the polymer melt and reinforcement units into the desired form and cooling the formed polymer composite so rapidly that the reinforcement units do not lose significantly their oriented internal structure.

One can manufacture also the self-reinforced absorbable material of the invention by heating absorbable fibers, threads or corresponding structures in a pressurized mould in such circumstances that at least part of these structures are partially softened or melted of their surface. Under the pressure the softened or melted surfaces of fibers, threads or corresponding structures are coalesced together and when the mould is cooled a self-reinforced composite structure is obtained. By a careful control of heating conditions it is possible to process composite samples where the softened or melted surface regions of fibers, threads or corresponding units are very thin and therefore the portion of oriented fiber structure is very high leading to materials with high tensile, shear, bending and impact strength values.

The above manufacturing principles can be applied when the self-reinforced absorbable materials are manufactured by batch processes (such as compression moulding and transfer moulding) or by continuous processes (such as injection moulding or extrusion or pultrusion).

Typical properties of the materials of this invention are the high content of oriented fibers bound together with thin matrix polymer layers between fibers, low porosity, smooth and compact surface, which all properties are obtained as a consequence of application of pressure and possibly also of heat during the manufacturing of the material. Good internal adhesion properties in combination with the above advantageous structural factors give for the material excellent mechanical strength properties such as high tensile, bending, compression or impact strength.

It is natural that the self-reinforced absorbable surgical material can include, in addition to matrix and reinforcement unit polymer, necessary additives, like colours, powder-like fillers or other additives.

The self-reinforced materials of the invention can be applied in osteosynthesis implants like in surgical devices or as their components in the form of plates, pins, nails, medullary rods, screws or in the form of other three-dimensional solids. The material can form also at least part of an osteosynthesis implant. It is natural that the at least partially absorbable matrix and/or reinforcement units can contain additives such as colours, antioxidants, plasticizers, lubricants, fillers etc. which are needed in processing of the material or to modify its properties or the properties of matrix and/or reinforcement units.

When the self-reinforced material is applied as a part of surgical plate, pin, rod etc. the self-reinforced structure may form e.g. the core of the device and the surface of the device can be prepared from other material. In this way the excellent mechanical properties of self-reinforced material can be combined with properties of other absorbable materials (such as slow absorption rate).

The self-reinforced material of the invention can be applied also in several other ways in combination with other absorbable and/or biostable materials. E.g. the mechanical properties of self-reinforced material can be modified by embedding into it absorbable reinforcing units with other hydrolytic properties than those of the self-reinforced material. Composites with excellent mechanical properties are also achieved when hybrid composites of self-reinforced materials with biostable fibers (such as carbon fibers) are manufactured.

The following non-limiting examples illustrate the present invention.

#### 50 Example 1

The melt of glycolide/lactide (90/10) copolymer (internal viscosity  $[\eta] = 1.5$  in 0.1 % hexafluoroisopropanol solution ( $T = 25^\circ\text{C}$ )) was mixed with the continuous fibers of the same material. The melt - fiber mixture was formed rapidly to cylindrical samples (diameter 4.5 mm) which were cooled rapidly and whose fiber content was 30 % (w/w). The tensile strength of these self-reinforced absorbable composite rods was 260 Mpa. The tensile strength of corresponding non-reinforced rods manufactured from glycolide/lactide copolymer melt was 50 Mpa.

#### 60 Example 2

Glycolide/lactide copolymer sutures (Vicryl®) (size 2 USP) were heated in vacuum at  $185^\circ\text{C}$  for 6 min which caused the partial melting of fiber units of sutures. The material was compression moulded into a cylindrical mould with a pressure of 2000 bar and it was cooled rapidly. The bending strength of these self-reinforced rods

was 170 Mpa. The bending strength of corresponding non-reinforced rods manufactured from glycolide/lactide copolymer melt was 90 Mpa.

5

### Example 3

Polyglycolide sutures (Dexon®) (size 2 USP) were heated in pressurized cylindrical mould (length 70 mm, diameter 4.5 mm) at 218°C for 5 min with a pressure of 2000 bar. The softened fiber material was fused partially together and the mould was cooled to room temperature rapidly. The tensile strength of these self-reinforced absorbable composite rods was 380 Mpa. The tensile strength of corresponding non-reinforced rods manufactured from polyglycolide melt was 60 Mpa.

15

### Example 4

Polyglycolide sutures (Dexon®) (size 2 USP) were melted at  $T = 230^{\circ}\text{C}$ . The polymer melt and corresponding continuous sutures (Dexon®) were mixed rapidly together, formed to cylindrical rods (diameter 3.2 mm) and cooled rapidly. The fiber content of self-reinforced rods was 40 % (w/w). Their tensile strength was 290 Mpa. The tensile strength of corresponding non-reinforced rods manufactured from polyglycolide melt was 60 Mpa.

### Example 5

Isomers which can be applied to manufacture absorbable osteosynthesis devices are e.g. isomers of polylactide like poly-L-lactide (PLLA) and the DL isomer (meso lactide). PLLA is crystalline polymer with the melting point 180°C and the DL isomer is amorphous polymer. The self-reinforced material can be manufactured of these materials by combining DL isomer matrix and PLLA fiber, thread or corresponding reinforcement unit structures to each other by means of heat and pressure.

Bundles of poly-L-lactide (PLLA) fibers (fiber diameter 12  $\mu\text{m}$ , amount of fibers in a slightly twisted bundle = 200 pcs, molecular weight of PLLA = 100 000) and the finely powdered DL isomer (meso lactide) (molecular weight = 100 000) were mixed mechanically together and compression moulded at 165°C and 2000 bar pressure for 6 min and cooled rapidly. The fiber content of self-reinforced rods was 50 % and their tensile strength was 300 Mpa. Tensile strengths of non-reinforced rods manufactured from polymer melts were: PLLA 60 Mpa and mesolactide 55 Mpa.

40

### Example 6

Self-reinforced rods of Example 3 were coated in injection moulding mould with 0.2 mm thick layer of poly-p-dioxanone melt ( $[\eta] = 0.8$  in 0.1 % tetrachloroethane solution ( $T = 25^{\circ}\text{C}$ ),  $T_m = 110^{\circ}\text{C}$ ) giving cylindrical, coated self-reinforced rods with the diameter of 4.9 mm. The bending strength of rods was 330 Mpa. After hydrolysis of three weeks in distilled water ( $T = 37^{\circ}\text{C}$ ) the coated self-reinforced rods had the bending strength 160 Mpa while the bending strength of non-coated self-reinforced rods was 90 Mpa.

50

### Example 7

Poly-L-lactide ( $M_w = 100\ 000$ ) fibers (diameter 12  $\mu\text{m}$ ) were heated in pressurized cylindrical mould (length 70 mm, diameter 4.5 mm) at 180°C for 7 min with a pressure of 2000 bar. The softened fiber material was fused partially together and the mould was cooled to room temperature rapidly. The tensile strength of these self-reinforced absorbable composite rods was 270 Mpa. The tensile strength of corresponding non-reinforced rods manufactured from poly-L-lactide melt was 50 Mpa.

60

### Example 8

Poly- $\beta$ -hydroxybutyric acid ( $M_w = 80\ 000$ ) fibers (diameter 15  $\mu\text{m}$ ) were heated in pressurized cylindrical mould (length 70 mm, diameter 4.5 mm) at 175°C for 5 min with a pressure of 2000 bar. The softened fiber material was fused partially together and the mould was cooled to room temperature rapidly. The tensile

strength of these self-reinforced absorbable composite rods was 200 Mpa. The tensile strength of corresponding non-reinforced rods manufactured from poly- $\beta$ -hydroxybutyric acid melt was 40 Mpa.

5

**Example 9**

Polydioxanone sutures (PDS of Ethicon) (Size 0) were heated in pressurized cylindrical mould (length 70 mm, diameter 4.5 mm) at 103°C for 6 min with a pressure of 2000 bar. The softened fiber material was fused partially together and the mould was cooled to room temperature rapidly. The shear strength of these self-reinforced absorbable composite rods was 140 Mpa. The shear strength of corresponding non-reinforced rods manufactured from polydioxanone melt was 50 Mpa.

15

**Example 10**

Polyesteramide (with the chemical formula VI, where  $R_1 = R_2 = -(CH_2)_{12}-$ ;  $M_w = 60\,000$ ) fibers (diameter 12  $\mu m$ ) were heated in pressurized cylindrical mould (length 70 mm, diameter 4.5 mm) at 105°C for 4 min with a pressure of 2000 bar. The softened fiber material was fused partially together and the mould was cooled to room temperature rapidly. The shear strength of these self-reinforced absorbable composite rods was 140 Mpa. The shear strength of corresponding non-reinforced rods manufactured from polyesteramide melt was 50 Mpa.

25

**Example 11**

Polyglycolide sutures (Dexon®) (Size 2) mixed with 10 wt-% of carbon fibers (with diameter 6  $\mu m$ ) were heated in pressurized cylindrical mould (length 70 mm, diameter 4.5 mm) at 218°C for 5 min with a pressure of 2000 bar. The softened polyglycolide fiber material was fused partially together and the mould was cooled to room temperature rapidly. The tensile strength of this self-reinforced absorbable hybride composite material containing carbon fibers was 450 Mpa. The tensile strength of the corresponding carbon fiber reinforced material manufactured from polyglycolide melt - carbon fiber mixture was 160 Mpa.

35

**Example 12**

Glycolide/lactide copolymer sutures (Vicryl®) containing 10 wt-% of polyglycolide sutures (Dexon®) (Size 2) were heated in vacuum at 185°C for 6 min which caused the partial melting of glycolide/lactide fiber units of Vicryl® sutures. The material was compression moulded in a cylindrical mould (length 70 mm, diameter 4.5 mm) with a pressure of 2000 bar and it was cooled rapidly. A hybride composite rod which was composed of self-reinforced glycolide/lactide material into which were embedded polyglycolide sutures was obtained. The bending strength of hybride composite material was 240 Mpa. The bending strength of corresponding composite manufactured from glycolide/lactide copolymer melt reinforced with 10 wt-% of polyglycolide sutures was 150 Mpa.

50

**Example 13**

Monofilament sutures (size 0) manufactured from polyglycolide/trimethylenecarbonate copolymer (Maxon of Davis + Geck) were heated in a pressurized cylindrical mould (length 50 mm, diameter 3.2 mm) at 180°C for 8 min with a pressure of 2000 bar. The sutures were partially fused together and the mould was cooled to room temperature rapidly. Self-reinforced absorbable rods with the shear strength of 110 Mpa were obtained. The shear strength of corresponding non-reinforced rods manufactured from totally melted Maxon sutures was 60 Mpa.

60

**Claims**

1. Surgical, osteosynthesis composite material which is at least partially absorbable in tissue conditions, characterized in that the osteosynthesis material is self-reinforced i.e. it is formed about the absorbable

65



polymer or copolymer matrix which is reinforced with the absorbable polymeric reinforcement units which have essentially the same chemical element percentage composition as the matrix has.

2. Osteosynthesis material as claimed in Claim 1, characterized in that the reinforcement units are in the form of fibers, threads, twists, cords, films, ribbons, woven fabrics or corresponding.

5 3. Osteosynthesis material as claimed in Claims 1 and 2, characterized in that the absorbable matrix and reinforcement units are manufactured of polyglycolide or of its copolymer.

4. Osteosynthesis material as claimed in Claims 1 and 2, characterized in that the absorbable matrix and reinforcement units are manufactured of polylactide or of its copolymer.

10 5. Osteosynthesis material as claimed in Claims 1 and 2, characterized in that the absorbable matrix and reinforcement units are manufactured of glycolide/lactide copolymer.

6. Osteosynthesis material as claimed in Claims 1 and 2, characterized in that the absorbable matrix and reinforcement units are manufactured of poly- $\beta$ -hydroxybutyric acid.

7. Osteosynthesis material as claimed in Claims 1 and 2, characterized in that the absorbable matrix and reinforcement units are manufactured of polydioxanone.

15 8. Osteosynthesis material as claimed in Claims 1 and 2, characterized in that the absorbable matrix and reinforcement units are manufactured of polyvinylalcohol.

9. Osteosynthesis material as claimed in Claims 1 and 2, characterized in that the absorbable matrix and reinforcement units are manufactured of polyesteramide.

20 10. Osteosynthesis material as claimed in any of Claims 1 - 9, characterized in that the material forms in the shape of a three-dimensional solid, an osteosynthesis implant, such as plate, pin, nail, medullary rod, screw, balk or like, or the material forms at least part of an osteosynthesis implant.

25 11. Method for manufacturing material for osteosynthesis devices in accordance with Claims 1 - 10, characterized in that the part of the material which will form the matrix is subjected to heat and/or pressure in such a way that the physical condition of the part of material which will act as matrix phase allows the development of adhesion between the nearby reinforcement units and the matrix.

12. A method for manufacturing material as claimed in Claim 11, characterized in that the melt of absorbable polymer or copolymer and the absorbable reinforcement units are mixed together, the mixture is formed into the desired shape and cooled down.

30 13. A method for manufacturing material as claimed in Claim 11, characterized in that the absorbable fiber, thread, twist, cord, film, ribbon, woven fabric or corresponding material is heated in such a way that the material is softened or melted and coalesced at least partially and the material is formed into the desired shape by means of pressure and cooled down.

## 35 Patentansprüche

40 1. Chirurgisches Kompositmaterial zur Osteosynthese, welches Material unter Gewebebedingungen mindestens teilweise resorbierbar ist, dadurch gekennzeichnet, dass es eigen-verstärkt ist, d.h., dass es auf einer resorbierbaren Copolymermatrix beruht, die selbst durch Elemente im wesentlichen die gleiche prozentuale atomare Zusammensetzung wie die Matrix zeigen.

2. Kompositmaterial gemäss Patentanspruch 1, dadurch gekennzeichnet, dass die Verstärkungselemente in Form von Fasern, Fäden, Garnen, Geflechten, Strängen, Schnüren, Schichten, Bändern, Geweben oder ähnlichem vorliegen.

45 3. Kompositmaterial gemäss Patentanspruch 1 oder 2, dadurch gekennzeichnet, dass die resorbierbare Matrix und die Verstärkungselemente aus Polyglycolid oder aus seinen Copolymeren hergestellt sind.

4. Kompositmaterial gemäss Patentanspruch 1 oder 2, dadurch gekennzeichnet, dass die resorbierbare Matrix und die Verstärkungselemente aus Polylactid oder aus seinen Copolymeren hergestellt sind.

50 5. Kompositmaterial gemäss Patentanspruch 1 oder 2, dadurch gekennzeichnet, dass die resorbierbare Matrix und die Verstärkungselemente aus Glycolid/Lactid-Copolymer hergestellt sind.

6. Kompositmaterial gemäss Patentanspruch 1 oder 2, dadurch gekennzeichnet, dass die resorbierbare Matrix und die Verstärkungselemente aus Poly- $\beta$ -hydroxybuttersäure hergestellt sind.

7. Kompositmaterial gemäss Patentanspruch 1 oder 2, dadurch gekennzeichnet, dass die resorbierbare Matrix und die Verstärkungselemente aus Polydioxanon hergestellt sind.

55 8. Kompositmaterial gemäss Patentanspruch 1 oder 2, dadurch gekennzeichnet, dass die resorbierbare Matrix und die Verstärkungselemente aus Polyvinylalkohol hergestellt sind.

9. Kompositmaterial gemäss Patentanspruch 1 oder 2, dadurch gekennzeichnet, dass die resorbierbare Matrix und die Verstärkungselemente aus Polyesteramid hergestellt sind.

60 10. Kompositmaterial gemäss einem der Patentansprüche 1 bis 9, dadurch gekennzeichnet, dass das Material ein dreidimensionales, festes Osteosynthese-Implantat bildet, und zwar in der Form von Platten, Stiften, Nadeln, Nägeln, Knochenmarksstäben, Schrauben, Balken u.ä., oder dass das Material mindestens einen Teil eines solchen Implantates bildet.

65 11. Verfahren zur Herstellung des Kompositmaterials gemäss den Patentansprüchen 1 bis 10, dadurch gekennzeichnet, dass derjenige Teil des Materials, welcher zur Matrix wird, Erwärmung und Druck ausgesetzt wird, und zwar so, dass seine physikalischen Eigenschaften dann die Verbindung mit den vorliegenden

Verstärkungselementen erlauben.

12. Verfahren gemäss Patentanspruch 11, dadurch gekennzeichnet, dass die Schmelze der resorbierbaren Homo- oder Copolymeren und die resorbierbaren Verstärkungselemente zusammen gemischt und die Mischung dann in der gewünschten Form abgekühlt und so verfestigt werden.

13. Verfahren gemäss Patentanspruch 11, dadurch gekennzeichnet, dass die resorbierbaren Fasern, Fäden, Garne, Geflechte, Stränge, Schnüre, Schichten, Bänder, Gewebe oder ähnliches so hoch erwärmt werden, dass die Materialien anschmelzen, worauf sie in die gewünschte Form gepresst und so abgekühlt und verfestigt werden.

## Revendications

1. Matériau composite chirurgical d'ostéosynthèse qui est absorbable, au moins partiellement, dans les conditions tissulaires, caractérisé en ce qu'il est auto-renforcé, c'est-à-dire qu'il est constitué par une matrice de polymère ou de copolymère absorbable qui est renforcée par des unités de renfort en polymère absorbable qui ont essentiellement la même composition en pourcentage d'éléments chimiques que la matrice.

2. Matériau d'ostéosynthèse selon la revendication 1, caractérisé en ce que les unités de renfort se présentent sous la forme de fibres, de fils, de fils retordus, de cordons, de films, de rubans, de tissus ou similaires.

3. Matériau d'ostéosynthèse selon la revendication 1 ou 2, caractérisé en ce que la matrice et les unités de renfort absorbables sont faites d'un polyglycolide ou d'un copolymère de celui-ci.

4. Matériau d'ostéosynthèse selon la revendication 1 ou 2, caractérisé en ce que la matrice et les unités de renfort absorbables sont faites de polylactide ou d'un copolymère de celui-ci.

5. Matériau d'ostéosynthèse selon la revendication 1 ou 2, caractérisé en ce que la matrice et les unités de renfort absorbables sont faites d'un copolymère glycolide/lactide.

6. Matériau d'ostéosynthèse selon la revendication 1 ou 2, caractérisé en ce que la matrice et les unités de renfort absorbables sont faites d'acide poly- $\beta$ -hydroxybutyrique.

7. Matériau d'ostéosynthèse selon la revendication 1 ou 2, caractérisé en ce que la matrice et les unités de renfort absorbables sont faites de polydioxanone.

8. Matériau d'ostéosynthèse selon la revendication 1 ou 2, caractérisé en ce que la matrice et les unités de renfort absorbables sont faites d'alcool polyvinylique.

9. Matériau d'ostéosynthèse selon la revendication 1 ou 2, caractérisé en ce que la matrice et les unités de renfort absorbables sont faites de polyesteramide.

10. Matériau d'ostéosynthèse selon l'une quelconque des revendications 1 à 9, caractérisé en ce qu'il constitue, sous la forme d'un solide tridimensionnel, un implant d'ostéosynthèse tel qu'une plaque, une cheville, un clou, une broche médullaire, une vis, une baguette ou similaires, ou il fait au moins partiellement partie d'un implant d'ostéosynthèse.

11. Procédé de fabrication d'un matériau pour des dispositifs d'ostéosynthèse selon l'une quelconque des revendications 1 à 10, caractérisé en ce que la partie du matériau qui formera la matrice est soumise à la chaleur et/ou à la pression, de telle façon que l'état physique de la partie du matériau qui servira de phase de matrice permette le développement d'adhérence entre les unités de renfort contiguës et la matrice.

12. Procédé de fabrication de matériau selon la revendication 11, caractérisé en ce que la masse fondue de polymère ou de copolymère absorbable et les unités de renfort absorbables sont mélangées ensemble, puis le mélange est mis sous la forme voulue et refroidi.

13. Procédé de fabrication de matériau selon la revendication 11, caractérisé en ce que le matériau sous forme de fibres, de fils, de fils retordus, de cordons, de films, de rubans, de tissus ou similaires est chauffé de telle manière qu'il soit ramolli ou fondu et aggloméré au moins partiellement, puis le matériau est mis sous la forme voulue par application de pression et refroidi.



ABSORBABLE  
FIBERS

ABSORBABLE  
MATRIX

